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SULPHUR AND METALS CAPTURE DURING COMBUSTION OF SYNCRUDE COKE IN A CIRCULATING FLUIDIZED BED COMBUSTOR

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December 1985

Project ERP-5.0.6.2.03
Circulating Bed Combustion

ENERGY RESEARCH PROGRAM
MINERAL SCIENCES LABORATORY
DIVISION REPORT ERP/MSL 85-158 (TR)

MICROMEDIA

Sulphur and Metals Capture During Combustion of Syncrude Coke in a Circulating Fluidized Bed Combustor

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INTRODUCTION

The Mineral Sciences Laboratory (MSL) of CANMET has been involved for several years in developing a method and in evaluating limestones as sorbents for SO2 capture in fluidized bed combustion. Limestone and dolomite samples from Nova Scotia, New Brunswick, and Alberta, as well as some from Sweden and Norway have been tested in a bench-scale fluidized bed reactor. A weighed, sized, quantity of sorbent is injected into a bed of sand fluidized at 850 C by a synthetic flue gas containing 0.3 % SO2. The equation of the resulting curve of sulphation versus time permits ranking of sorbents and also may be incorporated into a model for predicting the performance of sorbents in atmospheric fluid bed combustors. This unit can either test rock about 1 mm size as would be used in AFBC or pellets of powered limestone of the size used in CFBC. This research is documented in CANMET Divison reports (1,2).

Recently a pilot-scale circulating fluidized bed combustor has been designed, built and put into operation in MSL. The unit was built to investigate emissions of SO2, heavy metals, eg V,Ni, and alkali, eg Na,K, their capture with sorbents and their corrosive effects. This 100 mm diameter CFBC may be used to burn any finely ground fuel sulphide ores. An 8 kw electric heater and a 30kW propane burner are used for preheating the unit and for providing supplemental heat for low grade fuels. The first project for this unit is an investigation of the combustion of Syncrude by-product petroleum coke. This coke, a residue from the upgrading of oil sand bitumen by fluid coking, presents unique problems when considered for use as a fuel. It is relatively unreactive, has very high sulphur and heavy metal contents, very low volatiles and is difficult to grind. Previous papers have described CANMET sponsored work on this fuel with the A. Ahlstrom Corp's pilot-scale trials in their Pyroflow circulating fluidized bed and also the bubbling bed work by Becker at Queen's.

The combustion of any fuel produces gaseous emissions and ash residue. The Syncrude fluid coke contains 6 to 8 % S as well as vanadium and nickel such that the ash is about 4 % V2O5 and 1.5 % NiO. There is some concern that the high vanadium content may result in accelerated metal corrosion in the combustor. Vanadic oxidation corrosion is well documented for boilers using residual fuel oils (3). However, the conditions in a fluidized bed combustor are very different from a conventional boiler. The combustion temperatures are much lower, 800 - 900 C, such that corrosive alkali metal sulphate compounds are less likely to form. Additionally the bed material is mostly calcined and partially sulphated limestone and consequently the internal

surfaces of the combustor are exposed to and coated with this material. Fluidized beds may suffer from corrosion and corrosion-erosion which is aggravated by the presence of calcium sulphate. This corrosion is generally assumed to be associated with low oxygen partial pressure and high sulphur partial pressure which may occur in the dense bubble phase of a bubbling bed combustor.

All the published information on corrosion in fluidized beds is based on work done in bubbling beds. No documented work has been found in the literature on circulating fluidized bed corrosion. Additionally little data exists on the behaviour of vanadium compounds during fluidized bed combustion of high vanadium fuels. An attempt at a material balance of vanadium in the Ahlstrom tests was not very successful (4). Better results were obtained in combustion trials of Syncrude coke conducted in Queens University's 0.155 sq m AFBC. In three tests an average of 92.3 % of the initial vanadium and 92.0 % of the nickel were accounted for in the bed ash, cyclone drain and the baghouse dust (5). Plass reported on successful combustion trials on fluid coke in Lurgi's pilot CFB but gave little detail (6). A recent paper by Johnson (7) this year discussed the combustion of asphaltene containing 1347 ppm vanadium in a circulation boiler. He quoted vanadium capture of 97 % from heavy fuel oil residue combusted in a fluid bed of a limestone. The vanadium was captured as calcium vanadate. In another test with petroleum coke, the pilot plant was completely dismantled after test and no evidence of vanadium disposition on the tubes or the alumina bed material was found. No work has been found on vanadium induced corrosion in either bubbling or circulating fbc.

Having perceived a potential problem with corrosion from the combustion of this fuel a series of tests are planned for our small circulating bed unit. Preliminary test were carried out to resolve initial operating problems and to optimize the system. The size and design of our system permits accurate material balances of both solids and gases. Corrosion probes will be installed to determine the nature of short term corrosion and the deposits. This paper describes our circulating fluidized bed combustor as well as some of the results and some of the problems.

CIRCULATING FLUIDIZED BED COMBUSTOR

General Description

The CFB test unit, as shown in Fig 1, consists of three main parts; the 152 mm (6 in) dia. dense bed section, the 100 mm (4 in) dia. combustor column and the high temperature cyclone with hot solids return leg. The smooth changeover of the diameter is given by the transition section. The dense bed section is simply a length of stainless steel pipe (6 in, Sch.40), while all the combustor sections are made from 100 mm i.dia ceramic tubes cast inside a steel shell. The sections are bolted together by means of flanges. The overall height of the combustor is 2.81 m but may be increased to 4.62 m to increase gas residence time. The entire combustor is suspended from the ceiling of the

laboratory. This type of support allows the combustor to expand freely when being heated and easy access to all parts of the combustor. A water-cooled heat exchanger followed by a baghouse are provided for cooling and cleaning of the exhaust gas.

Distributor and Plenum Chamber

The air to the combustor windbox is supplied by a Roots blower. An orifice meter is used to measure the air flow. The the pneumatic feed line and the bed drain are in a concentric arrangement, extending through the center of the plenum and distributor plate. The air distributor plate is made of 25 mm (1 in) thick mild steel plate, 203 mm dia., machined to give a conical concave bottom surface to faciltate drainage from the bed. Thirty-three air nozzles made from 5/16" stainless steel bolts, arranged on a triagular pitch, are used for dispersing the air uniformly in the bed. Each nozzle has a 3.2 mm dia. hole drilled in the axis and two 1.6 mm dia. holes drilled at right angle to it. This arrangement prevents the weepage of bed materials into the plenum and gives a more streamlined nozzle profile.

Dense Bed Section

The dense bed section is made of a length of nominal 6 inch type 304 stainless steel pipe with flanged ends. A chromel wire is wound around the outside to give 8 kW of electrical resistance heating for start up. The section is insulated with Fiberfrax blanket. Initially this dense bed section was a ceramic tube. It was surrounded by two half shell heaters which were held by castable insulation in a 12 inch diameter pipe. Unfortunately, the thermal stress caused the ceramic to crack. Also dust filled the space between the heaters and the tube which caused heater failures. It is recognized that the stainless section will eventually fail and at that time it will be examined as a corrosion specimen.

Three water-cooled heat extraction probes enter this dense bed via the distributor plate. Depending upon their length they can provide a heat exchange surface area between 400 and 900 cm . They are primarily used in combustion experiments for cooling and as corrosion test specimens. They can be removed for roasting trials where extra heat must be provided to sustain the reaction.

This dense bed region is provided to ensure a more stable operation of the circulating fluidized bed. The twofold increase in cross-sectional area and the diverted portion of the air to the secondary air inlets make it possible to operate this dense bed at 1/2 to 1/4 of the fluidizing velocity of the combustor column. This prevents the bed from being blown away at high fluidizing velocities, a phenomena known to occur when pneumatic transport is in effect which causes the bed to empty in a short period of time. Better lateral mixing and smaller wall effect is also expected from a bed with larger cross-sectional area. It will, in addition, prevent slugging from occurring; these considerations are especially important for a small scale

unit such as the present one.

The Transition

A gradual transition (half angle = 6.5^{o}) is introduced for a smooth changeover from the dense bed to the combustor column. Four large access ports are located in this section, equally spaced on the circumference and inclined at 45^{o} from the horizontal. Presently one is used for dust return, one for overbed feed, one for viewing and the remaining one is used as the propane burner port. The transition section was made by casting a magnesia-based high temperature refractory inside the steel shell with the aid of a mold.

The Column Sections

There are presently two flanged sections, each 910 mm (36 in) that make up the combustor column. This is soon to be expanded to four sections in order to increase the gas residence time. They are made by lining a steel shell (10 in pipe) with a ceramic tube (100 mm dia. alumina tube). The annular space is filled with a insulating refractory (Fiberfrax variform-B). Each section has three 19 mm dia. access ports arranged equispaced along the column axis and which are used for pressure, temperature and gas/solid sampling as well as corrosion specimens.

High Temperature Cyclone

The success of the circulating fluidized bed depends mainly on the performance of its solid collection device. It must be operated at close to the bed temperature and withstand the highly erosive environment without loss of efficiency. The cyclone is made from ceramic tubes cast inside a steel shell. A rectangular (18 mm by 62 mm i.d.) alumina tube enters the cyclone body tangentially. The internal diameter of the cyclone is 175 mm dia. The cyclone body was modified such that 150 mm below the bottom of the gas inlet, the diameter is reduced to 135 mm over a 150 mm length. This portion of the cyclone is 610 mm. The conical piece at the bottom is made of high temperature magnesia based cast refractory. The dust drain port is 58 mm in diameter.

The designed entry velocity of the gas to the cyclone is 25 to 55 m/s with a corresponding pressure drop of 35 to 175 mm water column. The designed maximium operating temperature is 1000 C.

Dust Recycle System

The dust collected by the cyclone is returned to the column at the transition section. A steel pipe (2 in) lined with a 32 mm dia. ceramic tube is used as solids return leg. This leg runs horizontally for 250 mm to provide a solids seal to prevent a back flow of gas up through the bottom of the cyclone. A section of the ceramic tube is replaced by a quartz tube of which a 100 mm section is exposed for visual observation of the

hot flowing solids. The dust entry into the the combustor column is by means of gravity, assisted by an air ejector. Directly opposite the dust return port is where the propane burner fires into the combustor. This arrangement minimized the flame impingement on combustor parts, and at the same time produces an intense mixing zone where both heat and mass transfer are excellent.

A screw feeder has recently been installed on the cyclone return line to permit a regulated removal of ash from the unit. The quantity withdrawn is proportional to the feed rate and thus prevents overloading the system with solids.

The designed solids circulation rate is 30-100 times the solids feed rate. This gives a mass flux across the column about 8-26 kgm^2 /s at typical operating conditions.

Material Feed System

Solids are generally fed pneumatically into the dense bed through a bubble cap made of a nominal 1/4 inch pipe cap with six 3.5 mm dia. holes around the circumference. A steel ball inside the cap serves as a check valve to prevent the bed material from weeping back into the feed line. The bubble cap is centered on the distributor and slightly elevated from the air nozzles. An external variable-speed helical feeder delivers the feed to the pneumatic pick-up. This feeder works well for a material such as Syncrude coke which has excellent flowing properties. An alternate feeder has been developed for very fine powder such as the ore concentrate (-75 um) or the limestone (-150 um) tested. It is a novel fluidizing feeder with a stroking jet entrainment device controlled by a timer relay. The fluid bed feeder is in turn fed by a variable speed screw feeder. The entire system is on a weigh balance. The feeder can provide consistent rates from 0.5 up to 30 kg/h.

Materials having particles larger than 0.5 mm can be fed overbed by gravity. This feed port is in the transition section, immediately above the dense bed region. The maximium size that can be fed this way is 5 mm. This feeder has a hopper and variable speed screw.

Water-cooled Heat Exchanger

A vertical shell and tube type heat exchanger made of mild steel is used to cool the exhaust gas to within the limit of the operation of the baghouse (200 C max.). The gas passes through the inside of the 25 mm (1 in) steel tubes, and the water circulates in the outer shell. Four drain taps allows the use of 1/4, 1/2, 3/4 or all of the 2.5 sq m heat exchange surface area as required. The water flow rate is measured by a rotameter. Inlet and outlet temperatures are also monitored by thermocouples.

Fabric Filter

The baghouse is purchased from American Air Filter of Canada

Ltd. It has nine bags made of 14 oz. Nomex felt with a total filter area of 4.7 m (50 ft). The bags are cleaned by pulsed air jets directed at the center of each bag. This design has no moving parts and thus longer service life is expected. The maximium continuous operating temperature for this fabric is given by the supplier as 200 C.

Propane Burner

A small propane burner, with a maximium output about 30 kW, has been designed and constructed. It is necessary for starting up operations as well as a supplimentary heat source when roasting ores with negligible heat contents. The flame is stablized with a small flow, about 0.5 l/min, of hydrogen to prevent blow out in the CFB environment.

The combustion products from this burner represent only 2-6 % of the total flow through the CFB combustor, thus no significant effect on the overall process is expected, with the exception of possible slight increase of NOx emmision levels.

Gas Analysis

The CFB test unit is equipped with gas analyzers for measuring the concentrations in the exhaust gases so that material balance calculations can be performed on the test runs. The following gas analyzers are installed :

Oxygen analyzer, Beckman, model # 755
CO/CO2 analyzer, Infared Industries, model IR-702
SO2 analyzer, Western Research, model 721A
SO2 analyzer, Beckman, model # 865

The Western Research analyzer was recently acquired. It operates on a UV system and is less susceptable to moisture than the Beckman SO2 IR analyzer. All analyzers are calibrated daily.

The gas sample is drawn through a Pall filter cartridge downstream of the hot cyclone by a vacuum pump. A refridgeration unit and a Purma-pure are installed in the line to remove moisture. Outputs from the analyzers along with the thermalcouple readings are gethered by a Taurus data processor and stored in a microcomputer. The instantaneous readings are displayed on the computer screen and the two-minute running averages are printed out and also stored on the diskettes.

MATERIALS

Coke and Limestone Characteristics

Fifty tons of fluid coke were purchased from Syncrude in March, 1983. This material has been used in Queen's AFBC work, and the present work. An equal quantity of limestone was quarried about 50 km north of Fort McMurray. This sorbent is being used in conjunction with all the Syncrude tests. Analyses of both materials are given in Table 1.

The coke for our work was sieved through a 20 Mesh (850 um)

screen to remove the occasional large pieces which would cause problems with the pneumatic feeder. The limestone was crushed in a jaw crusher, cone crusher and finally a hammer mill. It was sieved on a vibratory 35 Mesh (500 um) screen. Fifty per cent of the limestone passed 70 um. This is finer than that which would be used in large scale CFB units.

Table 1 - Analysis of Syncrude Fluid Coke

Proximate analysis, dry basis, mass %	
Ash	6.68
Volatile matter	6.79
Fixed carbon (by diff)	86.53
Ultimate Analysis, dry basis, mass %	
Carbon	82.40
Hydrogen	1.43
Sulphur	6.96
Nitrogen	2.12
Ash	6.68
Oxygen (by diff)	0.41
Calorific value	29.5 MJ/Kg

Ash composition, mass %

SiO2	41.3	TiO2	3.6
Al2O3	25.1	NiO	1.23
Fe2O3	10.9	V2O5	4.70
Other oxides	14.1		

Fort McMurray limestone composition, mass %

SiO2	13.56	MgO	0.0
Al2O3	3.31	SO3	1.36
Fe2O3	1.43	Na2O	0.0
TiO2	0.34	K2O	1.00
P2O5	0.14	BaO	0.10
CaO	41.23	SrO	0.02
LOI	35.15		

Sulphation Capacity of Limestone

Fort McMurray limestone, along with other sorbents from Alberta and the Maritimes, was evaluated for its ability to react with sulphur dioxide gas in a fluidized bed reactor. As a "coarse" rock of the size that would be common in a bubbling atmospheric fluid bed combustor, that is 1.00 - 0.84 mm, its sulphation capacity, or the conversion of CaCO3 to CaSO4, was 22%. This is in the typical range of most limestones. However, when the rock was crushed to minus 150 um, and pelletized to permit testing in the reactor, the sulphation capacity was about 60 %. It is felt that the sulphation capacity of the finely powdered limestone determined by this method will be indicative

of that which should be expected in a circulating fluid bed. In other words this limestone in a circulating system should be about three times as efficient as in a bubbling bed with no recycle.

EXPERIMENTAL RESULTS

As the circulating fluid bed unit is still in the start-up phase, there are few data to report. By trial and error we have learned to operate a CFB. Several design modifications have been made to improve the start-up electric heater, the recycle line configuration and to increase the length of the cyclone body. There have been two occasions where sintered agglomerates were formed in the cyclone prior to the changes.

Petroleum coke is a very unreactive fuel, having only 7 % volatiles. It was found to be very slow burning below about 850 - 900 C. Consequently, we found it necessary to combust a sub-bituminus coal to thoroughly preheat the entire combustor before switching over to the coke.

SO2 and Vanadium Capture

To date coke and limestone blended in a Ca/S ratio of 2 have been used in all the test runs. The gas velocity, calculated for the 100 mm dia sections, was 3.0 - 3.5 m/s. The SO2 capture was calculated from the air flow to the combustor, fuel feed rate and the gas analyser data. Three tests have yielded 87.6, 89.4, and 90.4 %. We have chemical analysis for only one run of about 3.5 h duration. The collected data on the bed, cyclone, heat exchanger and bag house materials are given in Table 3.

Table 3. Material Balance of Test Run 291085

IN (mass g)		V	Ni	Ca	S	V/Ni
Initial bed	8000g	8.00	3.20	1701	553	2.50
Coke	8300	15.10	5.48	-	564	2.76
Limestone	4980	0.05	-	1467	-	-
OUT						
Bed	1755	1.23	0.40	210	62	3.08
Cyclone	4077	4.48	1.60	1017	384	2.80
Heat ex	5773	8.66	3.46	1425	480	2.50
Bag house	2640	7.66	3.70	571	149	2.07
% In/Out		95.4	105.5	98.3	95.4	

The material balance for the elements listed is very good, and would imply little, if any, loss of vanadium and nickel. The sulphur capture from this analysis, 95 %, is better than that calculated from the gas analyser, 89 %.

Corrosion

Although most of the combustor is lined with ceramic, the expanded bed section is stainless steel and there are some unlined pipe fittings on the dust return leg. Scale spalled from these metal parts was separated magnetically from the drained bed material. After examining under a microscope to ensure only scale was present, a sample was analysed for Ca, S, and V. The results were Ca 1.35 %, S 1.5 % and V 0.05 %. Subsequent examination of the 6 inch 304 SS section did not exhibit scaling therefore the scale appears to have come from the steel elbow and other fittings. The original steel should not contain vanadium.

During this period of starting up and learning how to operate the system corrosion probes were not present. To date the combustor has been operated for about 200 h, of which about 50 h were with coke. The dense secton is maintained at 700 C continuously by the electric heaters when there are no tests being run. Thermocouples, sheathed in 1/4 inch annnealed 304 stainless steel extending horizontally into the 100 mm section, were removed and examined. There was a deposit of loose quartz and ash material on the top of the tubes. On the bottom was a tan - brown, somewhat glass-like, deposit. The thermocouples were at several hundred C when removed and upon cooling started to spall. The spalled deposit was collected and although there was insufficient material for a detailed analysis Ca was analysed at 19.6 % and V was 0.42 %. The thermocouples were then abraded with fine sand paper. The loose deposit on the top was easily removed but that portion of the bottom deposit which had not spalled was very tenacious. There was one small area of corrosion pitting evident under the scale on the top of one of the thermocouples.

Nature of Vanadium

In petroleum coke, vanadium and nickel exist as complex porphyrins. After combustion the vanadium reportedly exists in the gas phase as oxides and hydroxides (8). These gases may react with other compounds or elements in the system. If sufficient reactive sodium were available, various sodium vanadates could result which have melting points as low as 560 C. Vanadium pentoxide melts at 690, and could condense on cooler metal tube and supports. If, however, there is an excess of calcium oxide, as would be the case in a fluidized bed, then thermodynamically the vanadium should form a calcium vanadate, presumably $3CaO.V_2O_5$ with a melting point of 1380 C. Any sodium present should preferentially react with sulphur dioxide to produce sodium sulphate. Under these conditions the vanadium should be harmless and not add to the corrosion.

Although it was suggested that upon combustion the vanadium will be in the gas phase, an examinaton of the ash shows vanadium to be present. Samples of coke ashed at 700,850 and 950 C in a muffle furnace were examined by ESCA. Photomicrographs of the ash shows a decrease in mass and volumn with increasing temperature. All of the samples contained 11 - 16 % carbon indicating incomplete combustion.

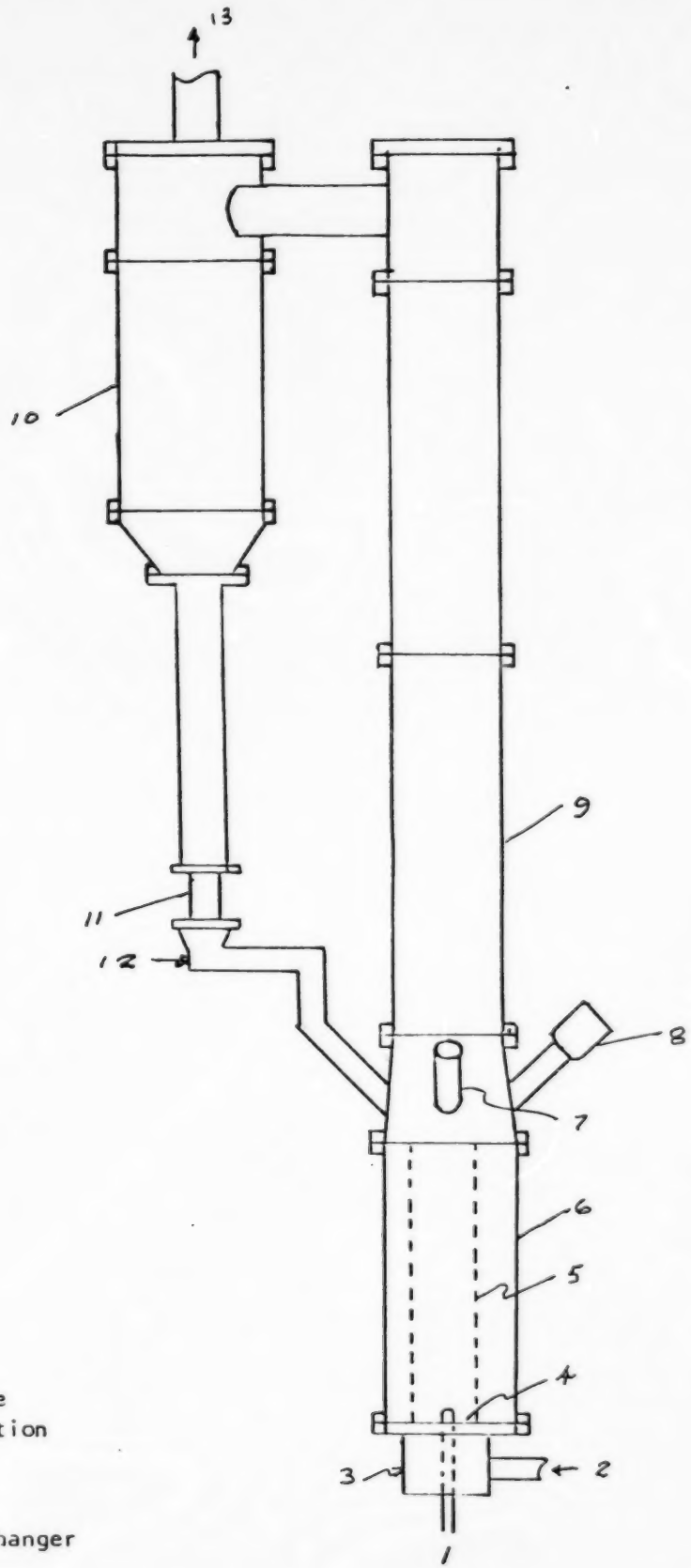
Comparison of the bulk sample analysis and the ESCA, which analysis the surface to a depth of 20 A or so, are presented in Table 2. The later results indicate that at higher temperatures, the vanadium, in the form of pentoxide, concentrates near the surface of the ash particle whereas the sodium appears to be depleted near the surface. There was insufficent nickel for the ESCA to detect although titanium was detected and was found to follow the same trend as the vanadium.

Table 2. Analysis of Ash

Ashing Temperature	Bulk Analysis		ESCA Analysis		
	V	Na	V	Ti	Na
700 C	2.32	1.36	1.0	tr	0.5
850 C	2.85	1.59	4.6	0.8	0.6
950 C			5.0	1.2	0.6

CONCLUSION

These preliminary results indicate that Syncrude coke can be combusted without significant problems. The small circulating fluid bed is now operational and should be capable of providing some reasonable data on combustion, emissions capture and corrosion.



1-pneumatic feed
2-fluidizing air
3-windbox
4-distributor
5-150 mm tube
6-electric heater
7-sight port
8-propane burner
9-100 mm ceramic tube
in castable insulation
10-cyclone
11-quartz sight tube
12-air ejector
13-exhause to heat exhanger
and bag house

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